Article

Contrasting Sources and Related Metallogeny of the Triassic and Jurassic Granitoids in the Chifeng–Chaoyang District, Northern Margin of the North China Craton: A Review with New Data

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1. Analytical Methods

1.1. Zircon LA-ICP-MS U-Pb Dating

Zircon separation was performed at the Shougang geological exploration institute, Beijing. Conventional heavy-liquid and magnetic techniques were employed followed by handpicking under a binocular microscope. The grains were mounted onto an epoxy resin disk, which was then polished to expose their cores. After the grains were examined and photographed under transmitted and reflected light, their internal structures were studied via cathodoluminescence (CL) at Beijing GeoAnalysis co., Ltd., prior to zircon U-Pb dating.

U-Pb dating and trace element analysis of zircon were simultaneously conducted by LA-ICP-MS at the Wuhan SampleSolution Analytical Technology Co., Ltd., Wuhan, China. Detailed operating conditions for the laser ablation system and the ICP-MS instrument and data reduction are the same as description by [90]. Laser sampling was performed using a GeolasPro laser ablation system that consists of a COMPexPro 102 ArF excimer laser (wavelength of 193 nm and maximum energy of 200 mJ) and a MicroLas optical system. An Agilent 7700e ICP-MS instrument was used to acquire ion-signal intensities. Helium was applied as a carrier gas. Argon was used as the make-up gas and mixed with the carrier gas via a T-connector before entering the ICP. A "wire" signal smoothing device is included in this laser ablation system [91]. The spot size and frequency of the laser were set to 32 μm and 5 Hz, respectively, in this study. Zircon 91500 and glass NIST610 were used as external standards for U-Pb dating and trace element calibration, respectively. Each analysis incorporated a background acquisition of approximately 20–30 s followed by 50 s of data acquisition from the sample. An Excel-based software ICPMSDataCal was used to perform off-line selection and integration of background and analyzed signals, time-drift correction and quantitative calibration for trace element analysis and U-Pb dating [92,93]. Concordia diagrams and weighted mean calculations were made using Isoplot/Ex_ver3 [94].

1.2. Whole rock major and trace elements

Eight granite porphyries samples were analyzed for their geochemistry. Whole-rock samples were trimmed to remove weathered surfaces, cleaned with deionized water, crushed, and then pulverized to ~200 mesh size in an agate mill. Whole-rock major element analyses were conducted on XRF (Primus II, Rigaku, Japan) at the Wuhan Sample solution Analytical Technology Co., Ltd., Wuhan, China with analytical uncertainties ranging from 1 to 3%. The detailed sample-digesting procedure was as follows: (1) Sample powder (200 mesh) were placed in an oven at 105 °C for drying of 12 h; (2) ~1.0g dried sample was accurately weighted and placed in the ceramic crucible and then heated in a muffle furnace at 1000 °C for 2 h. After cooling to 400 °C, this sample was placed in the drying vessel and weighted again in order to calculate the loss-on-ignition (LOI). (3) 0.6 g sample powder was mixed with 6.0 g cosolvent ($Li_2B_4O_7$: $LiBO_2$: LiF = 9: 2: 1) and 0.3 g oxidant (NH_4NO_3) in a Pt crucible, which was placed in the furnace at 1150 °C for 14 min.

Then, this melting sample was quenched with air for 1 min to produce flat discs on the fire brick for the XRF analyses.

For trace element components, the detailed sample-digesting procedure was as follows: (1) Sample powder (200 mesh) were placed in an oven at 105 °C for drying of 12 h; (2) 50 mg sample powder was accurately weighed and placed in a Teflon bomb; (3) 1 mL HNO_3 and 1 mL HF were slowly added into the Teflon bomb; (4) Teflon bomb was putted in a stainless steel pressure jacket and heated to 190 °C in an oven for >24 h; (5) After cooling, the Teflon bomb was opened and placed on a hotplate at 140 °C and evaporated to incipient dryness, and then 1 mL HNO_3 was added and evaporated to dryness again; (6) 1 mL of HNO_3, 1 mL of MQ water and 1 mL internal standard solution of 1 ppm In were added, and the Teflon bomb was resealed and placed in the oven at 190 °C for >12 h; (7) The final solution was transferred to a polyethylene bottle and diluted to 100 g by the addition of 2% HNO_3 for analyzing with Agilent 7700e ICP-MS. The precision was generally better than 5% for most trace elements according to duplicate analyses on these standards.

1.3. Whole rock Sr isotope ratio analyses

All chemical preparations were performed on class 100 work benches within a class 1000 over-pressured clean laboratory. Sample digestion: (1) Sample powder (200 mesh) were placed in an oven at 105 ℃ for drying of 12 h; (2) 50–200 mg sample powder was accurately weighed and placed in an Teflon bomb; (3) 1–3 mL HNO_3 and 1–3 mL HF were added into the Teflon bomb; (4) Teflon bomb was putted in a stainless steel pressure jacket and heated to 190 ℃ in an oven for >24 h; (5) After cooling, the Teflon bomb was opened and placed on a hotplate at 140 ℃ and evaporated to incipient dryness, and then 1 mL HNO_3 was added and evaporated to dryness again; (6) The sample was dissolved in 1.5 mL of 2.5 M HCl. Column chemistry**:** After centrifugation, the supernatant solution was loaded into an ion-exchange column packed with AG50W resin. After complete draining of the sample solution, columns were rinsed with 2.5 M HCl to remove undesirable matrix elements. Finally, the Sr fraction was eluted using 2.5 M HCl and gently evaporated to dryness prior to mass-spectrometric measurement. The residue was rinsed with 10 mL of 4.0 M HCl and then the REE fraction was eluted using 10 mL of 4.0 M HCl. The REE solution was used to separate the Nd fraction by the Nd-column method.

For the Rb-rich sample, after the separation of the common ion-exchange column, the Sr fraction was separated again by the Sr-specific resin. The solution was first converted to the HNO_3 media (3 M HNO_3). Then the solution was loaded into the Sr-specific resin and pre-conditioned with 6 M HCl and 3 M HNO_3. After complete draining of the sample solution, columns were rinsed with 3 M HNO_3 to remove undesirable matrix elements. Finally, Sr was eluted using MQ H_2O and gently evaporated to dryness prior to mass-spectrometric measurement.

Sr isotope analyses were performed on a Neptune Plus MC-ICP-MS (Thermo Fisher Scientific, Dreieich, Germany) at the Wuhan Sample Solution Analytical Technology Co., Ltd., Hubei, China. The Neptune Plus, a double focusing MC-ICP- MS, was equipped with seven fixed electron multiplier ICs, and nine Faraday cups fitted with 10^{11} Ω resistors. The faraday collector configuration of the mass system was composed of an array from L4 to H3 to monitor $^{83}Kr^{+}$, $^{167}Er^{++}$, $^{84}Sr^{+}$, $^{85}Rb^{+}$, $^{86}Sr^{+}$, $^{173}Yb^{++}$, $^{87}Sr^{+}$, $^{88}Sr^{+}$. The large dry interface pump (120 m^3 hr^{-1} pumping speed) and newly designed X skimmer cone and Jet sample cone were used to increase the instrumental sensitivity. Sr single element solution from Alfa (Alfa Aesar, Karlsruhe, Germany) was used to optimize instrument operating parameters. An aliquot of the international standard solution of 200 μg L^{-1} NIST SRM 987 was used regularly for evaluating the reproducibility and accuracy of the instrument. Typically, the signal intensities of ^{88}Sr in NIST SRM 987 were > ~4.0 V. The Sr isotopic data were acquired in the static mode at low resolution. The routine data acquisition consisted of ten blocks of 10 cycles (4.194 s integration time per cycle). The total time of one measurement lasted about 7 min.

The exponential law, which initially was developed for TIMS measurement [95] and remains the most widely accepted and utilized with MC-ICP-MS, was used to assess the instrumental mass discrimination in this study. Mass discrimination correction was carried out via internal normalization to a $^{88}Sr/^{86}Sr$ ratio of 8.375209 [96]. The interference elements Ca, Rb, Er, Yb have been completely separated by the exchange resin process. The remaining interferences of $^{83}Kr^{+}$, $^{85}Rb^{+}$, $^{167}Er^{++}$, $^{173}Yb^{++}$ were corrected based on the mothed described by Lin et al. (2016). One international NIST SRM 987 standard was measured every ten samples analyzed. Analyses of the NIST SRM 987 standard solution yielded $^{87}Sr/^{86}Sr$ ratio of 0.710244±22 (2σ, n=32), which is identical within error to their published values (0.710241±12) [97]. In addition, the USGS reference materials BCR-2 (basalt) and RGM-2 (rhyolite) yielded results of 0.705034±14 (2σ, n = 4) and 0.704192±10 (2σ, n = 4) for $^{87}Sr/^{86}Sr$, respectively, which is identical within error to their published values [98].

1.4. Whole rock Nd isotope ratio analyses

All chemical preparations were performed on class 100 work benches within a class 1000 over-pressured clean laboratory. Column chemistry: The REE solution from the Sr-column method was evaporated to incipient dryness, and taken up with 0.18 M HCl. The converted REE solution was loaded into an ion-exchange column packed with LN resin. After complete draining of the sample solution, columns were rinsed with 0.18 M HCl to remove undesirable matrix elements. Finally, the Sr fraction was eluted using 0.3 M HCl and gently evaporated to dryness prior to mass-spectrometric measurement.

Nd isotope analyses were performed on a Neptune Plus MC-ICP-MS (Thermo Fisher Scientific, Dreieich, Germany) at the Wuhan Sample Solution Analytical Technology Co., Ltd., Hubei, China. The Neptune Plus, a double focusing MC-ICP- MS, was equipped with seven fixed electron multiplier ICs, and nine Faraday cups fitted with 10^{11} Ω resistors. The faraday collector configuration of the mass system was composed of an array from L4 to H4 to monitor $^{142}Nd^{+}$, $^{143}Nd^{+}$, $^{144}Nd^{+}$, $^{145}Nd^{+}$, $^{146}Nd^{+}$, $^{147}Sm^{+}$, $^{148}Nd^{+}$, $^{149}Sm^{+}$, $^{150}Nd^{+}$. The large dry interface pump (120 m^3 hr^{-1} pumping speed) and newly designed X skimmer cone and Jet sample cone were used to increase the instrumental sensitivity. Nd single element solution from Alfa (Alfa Aesar, Karlsruhe, Germany) was used to optimize instrument operating parameters. An aliquot of the international standard solution of 200 μg L^{-1} JNdi-1 was used regularly for evaluating the reproducibility and accuracy of the instrument. Typically, the signal intensities of $^{144}Nd^{+}$ in JNdi-1 were > ~2.5 V. The Nd isotopic data were acquired in the static mode at low resolution. The routine data acquisition consisted of ten blocks of 10 cycles (4.194 s integration time per cycle). The total time of one measurement lasted about 7 min.

The exponential law, which initially was developed for TIMS measurement [60] and remains the most widely accepted and utilized with MC-ICP-MS, was used to assess the instrumental mass discrimination in this study. Mass discrimination correction was carried out via internal normalization to a $^{146}Nd/^{144}Nd$ ratio of 0.7219 [61]. The interference elements Sm have been completely separated by the exchange resin process. The remaining interferences of $^{144}Sm^{+}$ were corrected based on the mothed described by Lin et al. (2016). One JNdi-1 standard was measured every ten samples analyzed. Analyses of the JNdi-1 standard yielded $^{143}Nd/^{144}Nd$ ratio of 0.512118±15 (2σ, n = 31), which is identical within error to their published values (0.512115±07)[99]. In addition, the USGS reference materials BCR-2 (basalt) and RGM-2 (rhyolite) yielded results of 0.512644±15 (2σ, n=6) and 0.512810±15 (2σ, n = 4) for $^{143}Nd/^{144}Nd$, respectively, which is identical within error to their published values [98].

1.5. Zircon O-Hf isotopes

Zircon oxygen isotopes were measured using the SHRIMP II e-MC instrument in the Beijing SHRIMP Center, Institute of geology, Chinese Academy of Geological Sciences, Beijing, China. Detailed analytical processes are similar to those described by Dong et al. (2016) [100]. Oxygen isotopic measurements were made on the same zircon grains that had previously been analyzed for U-Pb. Each $^{18}O/^{16}O$ analysis took approximately 6 min and the analytical procedures and conditions were similar to those described by Ickert et al. (2008) [101]. The spots were about 30 μm in diameter. The reference material used for calibration of instrumental mass fractionation (IMF) was TEMORA 2 zircon ($\delta^{18}O$ = 8.20‰)[102].

In situ zircon Hf-isotopic analyses were performed at sites, or in the same age domains (identified used CL images), in the zircons used for U-Pb and O isotope analyses. Hf-isotopic analyses were undertaken using a New Wave UP213 laser-ablation microprobe, attached to a Neptune multi-collector ICP-MS at the institute of Geology, Chinese Academy of Geological Sciences, Beijing, China. Lu-Hf isotopic measurements were made with ablation pits 44 μm in diameter, a repetition rate of 8 Hz, a laser beam energy density of 10 J/cm^2, and an ablation time of 26 s. The detailed analytical procedures were similar to those described by Hou et al. (2007) [103]. Zircon GJ-1 was used as the reference standard during our routine analyses. The weighted mean $^{176}Hf/^{177}Hf$ ratio of GJ-1 (0.282007±25; 2σ) is similar to the commonly accepted weighted mean $^{176}Hf/^{177}Hf$ ratio of 0.282013±19 (2σ) reported for in-situ analysis by Elhlou et al. (2006) [104].